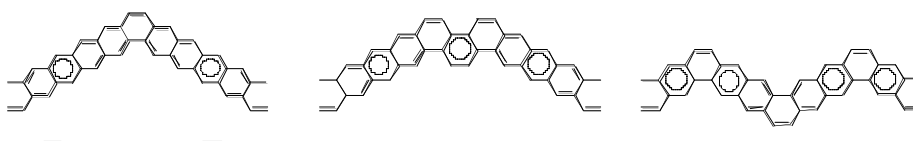


Possible Ring Structures of Armchair Single Walled Carbon Nanotube

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Energetics and the electronic structure of various types of single walled carbon nanotubes have been investigated by using Density Functional Theory and mainly Armchair [n,n], zigzag [n,0] and chiral [n,m] $C_{40}H_{20}$ nanotubes have been considered. Calculations show that the armchair isomer is the most stable among the three types known and they further reveal the factors that stabilize this isomer. Nucleus independent chemical shift calculations indicate the aromaticity of the individual hexagonal rings in the carbon nanotubes and through that explain the extent of electron delocalization in them.

Introduction

Extensive research had been conducted both experimentally and theoretically on carbon nanotubes (CNT) since their discovery by the electron microscopy¹. This discovery attracted physicists, chemists, nano technologists and material scientists in large numbers. More research has been devoted to their extraordinary electronic properties². Many reports have appeared in the literature related to thermal³, structural studies that showed clear dependence of the nanotube properties on their diameter, length and chirality⁴. Structures and aromaticity of finite-length armchair⁵ CNT and the reactivity of carboxylic groups on Armchair and Zigzag CNT⁶ have been reported. Clearly, the nanotube research has become a booming area since they were discovered. In this paper, we address specifically the stability, the layout of the ends and try to identify the factors that stabilize the isomers viz., armchair nanotubes($n=m$, $\text{chiral} \angle 30^\circ$), zigzag (n or $m = 0$, $\text{chiral} \angle 0^\circ$) and chiral ($n \neq m$, $\text{chiral} \angle 0-30^\circ$).

We have focused our interest on the energetics of the different geometries of armchair nanotube endings.

Computational Details

Density Functional Theory (DFT) calculations have been performed using GAUSSIAN03⁸, Revision C.02 on a cluster of AMD Opteron (tm) Processors 246, 2.0 GHB CPU. Geometry optimizations have been done at B3LYP/6-31G(d). After performing a geometry optimization, Natural Bond Orbital (NBO)⁹ analysis and NICS¹⁰ analysis have been carried out. NBO delocalization energetic analysis have been done using \$DEL keyword as implemented in Gaussian. Total binding energy of a system can be partitioned into Lewis (E_L -localized) and non-Lewis (E_{NL} - delocalized) contribution.

$$E_{NL} = E_{Tot} - E_L$$

The Rydberg and anti-bonding orbitals are the non-Lewis NBO orbitals that have star in their labels (Ry*, BD*) and they are deleted and NBO calculation performed. The difference in the energy of the system before and after deletion of anti-bonding terms provides an useful measure of the energy contribution due to the deleted terms. E_{NL} (Non-Lewis) energy is equivalent to $E_{deccloc}$ (delocalization energy). Using this approach, delocalization energy has been calculated.

NICS¹⁰ is a simple and useful measurement to characterize the aromaticity of molecules. NICS have been computed using Gauge Including Atomic Orbitals (GIAO) method at B3LYP/6-311+G(d,p) level that gives indices of the negative value of the magnetic shielding, computed at individual ring center NICS(0), at 1 Å distance above the individual ring center NICS(1) and at center of the nanotube. NICS depends not only on the π system but also on the other contribution of lone pairs, atoms and the circulation of electrons.

Results and Discussion

Possible ring structure of single walled carbon nanotubes(SWCNT) are drawn in Fig.1a and b.

The above structures differ in their geometry; difference is in the number of full benzenoid and repulsive hydrogen pairs. That is F, E and D have 5 aromatic rings but different number of repulsive hydrogen pairs such as 5, 4, 3 respectively. C and B have the same number of repulsive hydrogen pairs(2), but the number of full aromatic rings are 4, 3 respectively. The A form has 2 full aromatic benzene rings and 1 repulsive hydrogen pairs only. These results are listed in Table 1 along with their calculated relative energies, frontier orbital energy (FOE) gap and delocalization energy. The corresponding bond lengths are given in Table 2. The curvature effect of armchair SWCNT has been shown in Fig 2.

Calculated energy values show that the armchair isomer is the most stable. Choosing this isomer as reference, relative energies of other isomers are presented in Table 1. These values show that the A is the least stable one. E isomer is less stable by 2.1 kcal/mol than F. The difference in energy is due to the number of C=C outer bond (marked in figures as 'a') of the molecule. Optimized structures show that in all the isomers the bond labeled as 'a' measure 1.35 Å that is comparatively shorter than all other bonds. The bond labeled d (Fig.1c) that is connecting the two rings is much longer (1.452 Å) in F isomer and slightly higher for other isomers as shown in the Table 2. The Frontier Orbital Energy (FOE) gaps also reveal that their gap for the F isomer is higher than the other isomers.

We also have evaluated the curvature effect of the F nanotube since it is the most stable one. We have taken planar $C_{42}H_{24}$ molecule and calculations have been carried out at different radius and obtain a nice correlation with the mechanical strain model shown in Fig 2. The same work has already been done using band structure calculation¹¹ and our DFT result is in good agreement with their result.

However it is still not clear what factors influence the stability of the geometries. Thus, we have extended our calculation to find out the delocalization energy of the molecule. NBO has been used to evaluate the delocalization energy. According to the NBO procedure, calculations have been carried out for the all the geometries and the results are in good agreement with their total energies. The computed delocalization energies are presented in Table 1. It shows that F is the most stable one which has a delocalization energy of 2742.48 kcal/mole. The second most stable geometry is the E and the least stable one is A, which is 9537.81 kcal/mol above the F isomer.

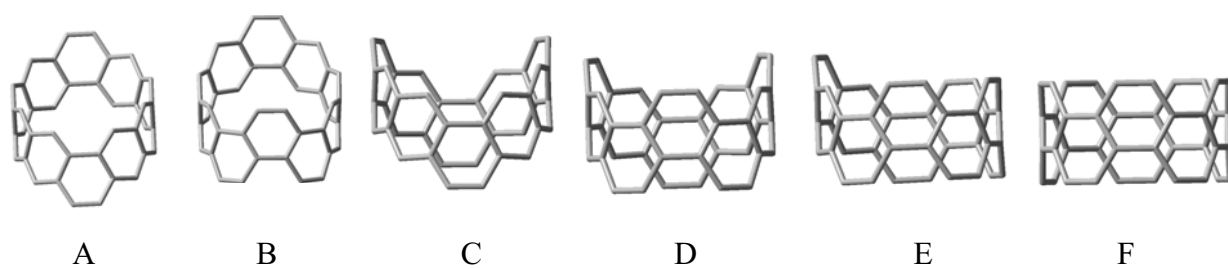
Positive NICSs denote antiaromaticity and negative NICSs denote aromaticity. Depending on the ring environment the NICSs value change as shown in the Fig. 1c. Calculations have been performed at the individual benzenoid rings at NICS (1) and the values are indicated in Fig. 1c. F isomer has five benzenoid rings, all rings fall in the same category α (-5.69 ppm) and it shows that F isomer is having high aromaticity. E isomer has three types of benzenoid rings which are called α (-6.43 ppm), β (-7.72 ppm) and γ (-5.71 ppm). Benzenoid ring β is more aromatic compared with α and γ . Like E isomer, D isomer also have three types of benzenoid rings in which β rings have the high aromatic value of -8.21 ppm. C and B isomers have only two types of benzenoid rings namely α and β in which β rings have NICS values of -7.34 ppm and -7.75 ppm respectively. The A isomer has two benzenoid ring and it all falls in the same category α (-7.45 ppm). NICS at center of the geometry reveals that it is a paratropic compound; the results are presented in Table 1. F isomer is less (14.24 ppm) paratropic compared with other isomer such as E (14.77 ppm), D (15.32 ppm), C (16.15 ppm), B (18.52 ppm) and A (27.27 ppm).

Conclusions

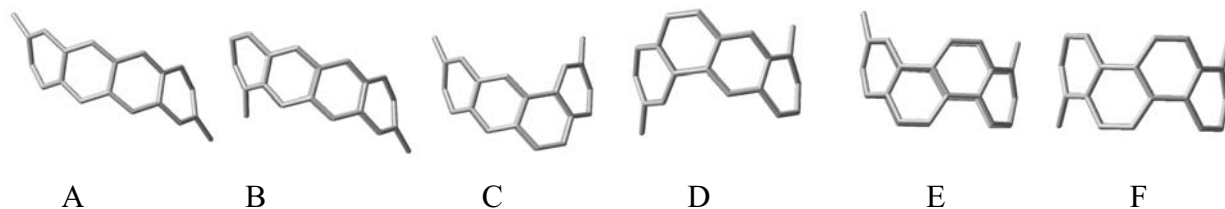
In summary, computed total energy, delocalization energy analysis, FOE gaps, NICS and the C-C bond length clearly confirm that the F structure is the most stable one. The other geometries are in the following decreasing order of stability $E > D > C > B > A$.

Acknowledgment

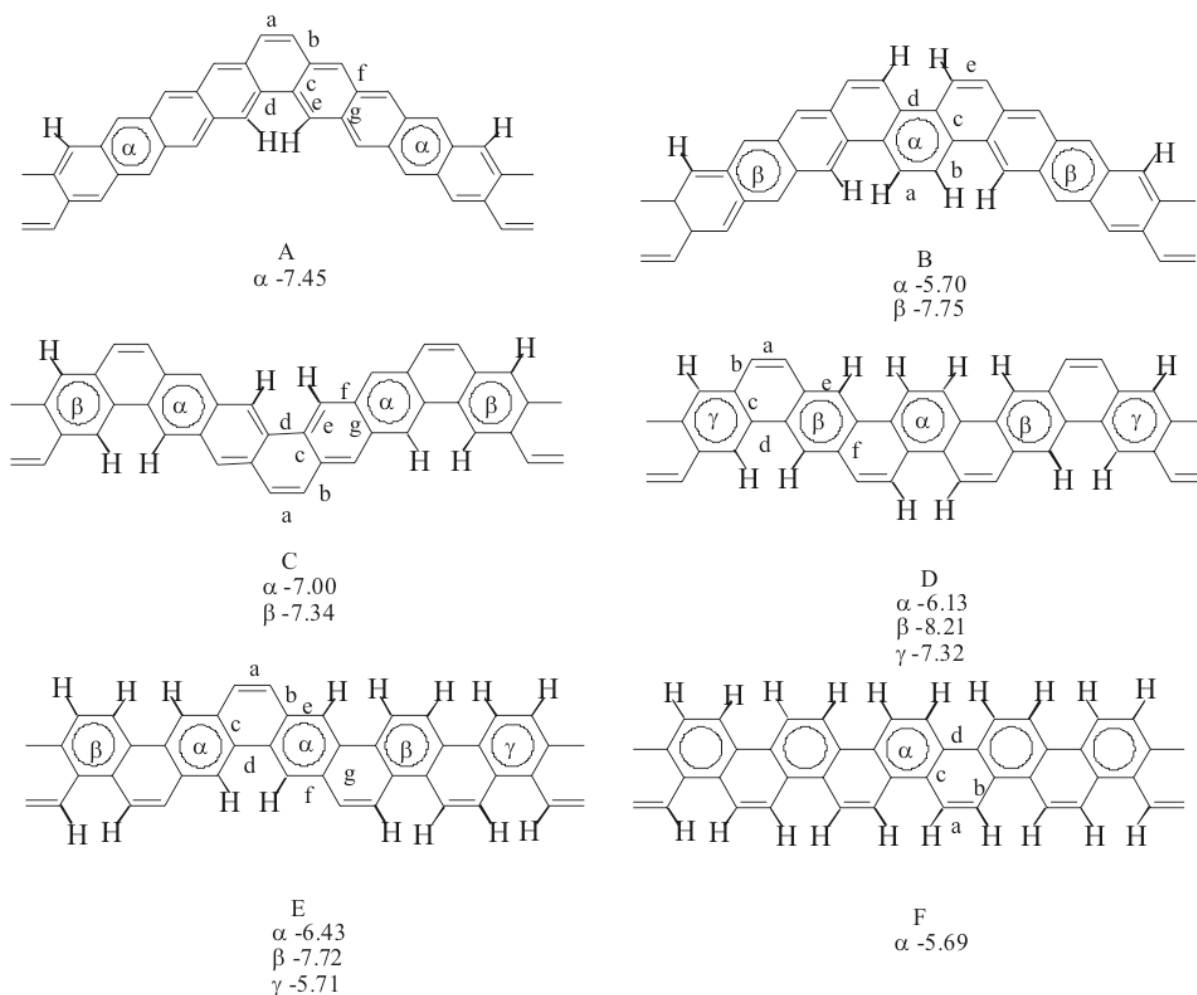
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a)



b)



c)

Fig.1. Schematic and Optimized structures of the $C_{40}H_{20}$ nanotubes a) Top view b) Side view c) Schematic representation NICS(1) values of the benzenoid rings α, β, γ are also indicated. Selected bond lengths a-g are referred in the text

Table 1: Calculated Relative Energy (kcal/mol), Frontier Orbital Energy gap (eV),
Delocalization Energy (kcal/mol) and NICS(1) (ppm) at the center of the SWCNTs

Isomer	No of full aromatic rings	No of repulsive H pairs	Relative energy	FOE gap	E _{deloc}	NICS at Center of the SWCNT
A	2	1	28.58	1.82	12380.29	-27.27
B	3	2	19.44	2.10	12019.96	-18.52
C	4	2	9.82	2.56	10664.50	-16.15
D	5	3	3.82	2.80	7578.06	-15.31
E	5	4	2.1	2.91	2757.50	-14.76
F	5	5	0.0	3.05	2742.48	-14.24

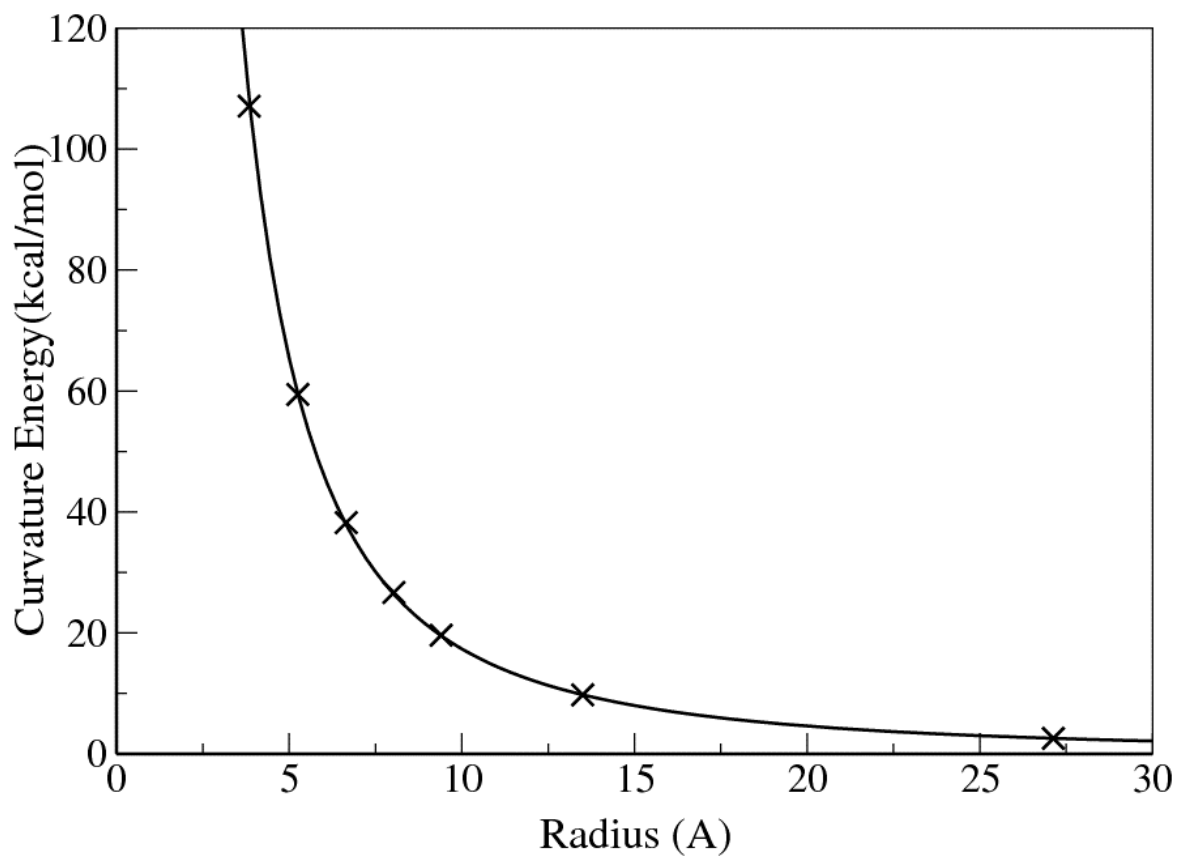


Fig 2. Curvature Effect on F isomer CNT

Table 2: Selected C-C Bond lengths (Å) in this SWCNTs

Isomer	a	b	c	d	e	f	g
A	1.349	1.460	1.487	1.459	1.375	1.434	1.449
B	1.349	1.450	1.450	1.486	1.373	-	-
C	1.350	1.457	1.447	1.484	1.391	1.420	1.436
D	1.354	1.451	1.430	1.474	1.40	1.430	-
E	1.354	1.452	1.433	1.476	1.399	1.407	1.430
F	1.366	1.435	1.412	1.452	-	-	-

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